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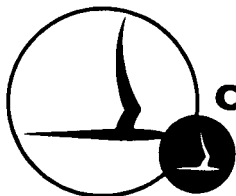
**RESONANCE ABSORPTION SPECTROPHOTOMETRY OF
THE HYDROGEN ATOM BEHIND SHOCK WAVES**

**By: A.L. Myerson, H.M. Thompson, and
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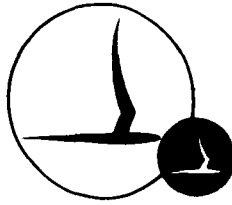
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FOREWORD

The studies presented in this report were sponsored by the National Aeronautics and Space Administration under Contract No. NASr-109 as part of a general study of nonequilibrium gasdynamics related to propulsion systems.

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LIST OF SYMBOLS

I_o	intensity of radiation of frequency ν at source
I_ν	intensity of source radiation signal at frequency ν after attenuation
k_o	absorption coefficient of gas at line center and frequency ν , for case of Doppler broadening
$k_{o,\nu}$	absorption coefficient of gas at line center corrected for Doppler and Lorentz broadening
P_H	partial pressure of atomic hydrogen
l	path-length through which radiation absorption takes place
δ	variable distance from point $\nu - \nu_o$; a variable over which integration is taken
$\Delta\nu_N$	natural half-breadth of the line
$\Delta\nu_L$	Lorentz half-breadth of the line
$\Delta\nu_D$	Doppler breadth of the line
f	oscillator strength of the line
M	molecular or atomic weight of absorbing species
$\bar{\nu}$	wave number, in cm^{-1} , of line center
T_2	temperature in $^\circ\text{K}$ behind incident shock
τ_r	relaxation time; defined as time required for I_o to attenuate to I_o/e
c_o	concentration of H_2 at time = 0 in moles/cc
c	concentration of H_2 at time t in moles/cc
c_M	total concentration of all species at time t in moles/cc
α	fraction of starting concentration of H_2 dissociated = $1 - c/c_o$
k_d	specific dissociation rate constant
k_r	specific recombination rate constant

X_{H_2}	mole-fraction of H_2 in starting gaseous mixture
t_p	particle time of gas behind incident shock
t_s	oscilloscope or laboratory time behind incident shock
$\alpha_{\tau_r}, \alpha_{eq}$	fraction of H_2 molecules dissociated at time τ_r and at equilibrium, respectively
P	probability factor of reaction rate theory
E	activation energy
$\bar{U} \left(= \frac{t_s}{t_p} \right)$	velocity of gas-flow relative to shock wave divided by velocity of shock wave
τ_f	electronic filter time constant

Note:

Arabic numbers refer to mathematical relations

Roman numerals refer to chemical reactions.

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ABSTRACT

The rate of formation of atomic hydrogen behind an incident shock wave in hydrogen-argon mixtures has been followed directly by means of atomic absorption spectrophotometry. The absorption involved the strong, resonance transition of the hydrogen atom from its ground state to the first excited level. The development of a cool, low pressure source of Lyman α radiation was required so that the half-width of the source line could be considered thin when compared with that of the same line in absorption arising from the hydrogen atoms behind the shock front. Preliminary rates have been calculated and provide evidence for dissociation catalyzed by oxygen.

author

I. INTRODUCTION

The present report describes the application of atomic resonance absorption spectrophotometry (hereafter a. r. a. s.) to the direct measurement of the changing concentration of atomic hydrogen behind shock waves. This has been achieved¹ by making use of the intense optical absorption arising from the electronic transition of the hydrogen atom from its ground state to the first excited level. This transition is known as Lyman α and occurs well down in the vacuum ultraviolet region of the spectrum at 1215.7 $\overset{\circ}{\text{A}}$. The atomic hydrogen was produced behind a shock wave in a rectangular cross section, shock tube. This approach was undertaken in order to make use of the improved accuracy provided by the high sensitivity of a. r. a. s. to atomic hydrogen concentration, the low sensitivity of the atomic spectrum to temperature and pressure changes and the fact that the technique is specific with respect to following the reaction product itself. These combined advantages are not available in any one of the techniques previously used for hydrogen rate measurements, the nature and status of which are reviewed later in this section.

A significant part of the evolution of the technique involved the development of a continuously operating, intense but cool source of Lyman α radiation which could be readily absorbed by the transition of the hydrogen atoms in the shock tube. The investigation as described herein brings the development of the technique to a point where feasibility is shown and preliminary rate measurements are described and interpreted. A brief description of the historical background and theoretical considerations is presented first in the following sections.

Dissociation Kinetics of the Homonuclear Diatomic Molecules

In the early fifties, interest began to increase rapidly in the non-equilibrium high temperature gas dynamics of homonuclear diatomic molecules. The problems of missile re-entry focussed research first on oxygen and nitrogen. At a later date, questions of missile propulsion began to concentrate attention on the kinetics of hydrogen. At the same time, the halogens began to receive considerable attention from a basic point of view because they provided tractable systems for observations of the fundamental mechanisms involved in the kinetics of the homonuclear diatomic molecules. The oxygen molecule has received the most attention because of its practical importance and the thermal and spectroscopic accessibility of its chemistry over a wide range of temperatures. For corresponding reasons of inaccessibility, nitrogen studies have been relatively sparse. Hydrogen and the halogens may be considered to fall more or less in the middle but hydrogen would appear to be in a phase of waxing interest because of its role in nuclear propulsion. In the case of nuclear propulsion, a knowledge of the nonequilibrium gasdynamics is vital to optimum conservation of recombination energy where hydrogen is the working fluid. The effect of dissociation rates on specific impulse and their catalysis by various species has been considered in detail by means of numerical solutions of coupled gas dynamic chemical kinetic systems.²

The techniques which have been used to measure the rates of dissociation and recombination at elevated temperatures fall into two categories: (1) the following of the density behind the shock wave, and (2) the measurement of the changing concentration of individual species. The literature on

the high temperature rates of oxygen and nitrogen has been critically covered by M. Bortner and J. Golden.³ Some of the initial shock-tube studies of halogen dissociation rates are represented by Refs. 4, 5, and 6. A more recent study of chlorine by means of rapid-response mass spectrometry is described in Ref. 7. The investigations of hydrogen dissociation kinetics at room and elevated temperatures are included among Refs. 8-20. The most popular technique used by investigators to follow the density behind a shock wave has been the application of interferometry, with X-ray densitometry in second place. These techniques have provided much interesting data but are not specific to the species under consideration. Thus their sensitivity to chemistry is strongly dependent on the conditions and composition of the gas.

The measurements of the concentrations of individual species, prior to the present work, have in all cases consisted of following the absorption spectra of the diatomic molecule. This method is thus specific and has, again, yielded significant results. However, the considerable sensitivity of the complex spectra of the diatomic molecules to temperature and pressure changes has to be taken carefully into account. Another technique,²¹ while concerned with free radicals such as OH and CN rather than homonuclear dissociation, is relevant here since it does follow the concentration of diatomic radicals behind shocks. Radiation from flash sources of specific transitions of the OH or CN spectra is absorbed by the same transition of the same species formed behind shock waves. The method is referred to by the authors as specific absorbimetry.

Status of Dissociation Rate Studies of Hydrogen

In the case of the hydrogen molecule, all three of the techniques mentioned have been used but with varying results. The data are spread over three orders of magnitude and disagree widely even for a given third body of recombination. Figure 1 is a graphical summary of the data for hydrogen in terms of the recombination rates, most of them calculated from dissociation rates measured at high temperatures. Also included are a number of room temperature and one high temperature recombination measurements made at considerably earlier dates by various other methods, many of them involving catalytic heating which is difficult to reproduce. It is clear that while significant steps have indeed been taken in the investigation of the high temperature nonequilibrium gasdynamics of hydrogen, considerable study remains to be done.

It has been the intent of the present program to follow the concentration behind the shock wave of the atomic species itself, in this case the hydrogen atom, by applying the technique of a. r. a. s. in the vacuum ultraviolet. The idea in principle is to create a spectroscopic system in which the light source emits the same resonance line frequency as is absorbed by the atom under investigation. This method of measuring reaction rates is specific with respect to the product and employs a spectrum inherently simple in nature. It simplifies significantly the spectrometric problem especially if the source line is thin compared with the absorbing line. Under such conditions, the spectrophotometer then functions only to isolate the Lyman α line from any neighboring lines. Wide slits can thus be used providing optimum conditions for high light intensity. The relative thinness of the source line can

be achieved if one uses a cool, low pressure light source and absorbing atoms which are in a hot, high pressure medium. The present report describes initial results obtained by meeting those conditions through the use of a continuously operating radiofrequency-powered source of Lyman α radiation at 1215.7\AA , which is absorbed by the hydrogen atoms forming behind a shock wave. The attenuation resulting from this absorption process is quite high and, in fact, is complete for values of P_H less than a micron under some conditions. The advantages and disadvantages of such high sensitivity and projected methods for decreasing it are discussed later in this report.

II. ATOMIC RESONANCE ABSORPTION SPECTROPHOTOMETRY OF THE HYDROGEN ATOM

Historical Background

The first and, as far as is known, only previous attempt to follow the chemical kinetics of atomic hydrogen by means of a. r. a. s. is that carried out by Preston²² in the late thirties. Attempts were made to follow recombining H atoms formed at room temperature by means of a discharge. A flash light source of Lyman α was used. While a change in atomic hydrogen concentration was noted, only surface recombination could be followed. Here it will be noted, the pressure-temperature ($P-T$) conditions of light source and absorbing system were inverse from those set up as the criteria in the present research. During this same period, most of the early quantitative work on a. r. a. s. was performed using mercury vapor²³ in equilibrium systems for the purposes of studying line shapes. The first application of a. r. a. s. using the $P-T$ criterion of source and absorber as discussed, to the absolute determination of the concentration of specific atomic species, is believed to be that of Vidale.²⁴ He applied a. r. a. s. to the measurement of the very small partial pressures of sodium and other atomic species over refractories in equilibrium in a high temperature furnace. While a. r. a. s. has, since that time, become a widely used and routine analytical tool for metals in flames (see Ref. 25 for a review of this application) it is there employed mostly through empirical calibration.

Theoretical Bases for the Experiments

The same spectroscopic principles employed by Vidale (loc. cit.) for equilibrium systems are valid for our non-equilibrium system. In

view of his discussion,²⁴ the theory will be only briefly reviewed. The equations and theory for line broadening are amply discussed in the classic books by Mitchell and Zemansky²³ and Tolansky.²⁶ The experiment, the details of which are described in the next section, consists of measuring the attenuation of the Lyman α radiation of a cool, low pressure light source by the hot atomic hydrogen formed behind a shock wave. The transition involved both for emission and absorption is known as Lyman α and takes place from the ground electronic state of the hydrogen atom to its first excited level ($1^2S \leftrightarrow 2^2P$). The attenuated signal I_ν , resulting from H atom absorption at a given wavelength ν and original intensity I_0 is given in terms of the absorption coefficient, the partial pressure of atomic hydrogen and the path length, by

$$I_\nu = I_0 e^{-k_{\nu} P_H l}$$

All symbols are defined in the list at the beginning of the report. As indicated previously, it is assumed that the source line is thin with respect to the absorbing line so that the absorption coefficient due to the hydrogen atom behind the shock can be calculated at the center of the line of the absorbing hydrogen atom. The two major sources of broadening behind the shock wave are Doppler, due to temperature, and Lorentz, due to pressure. Other types of broadening such as Holtzmark, Stark and natural may be neglected under the present conditions for reasons of low hydrogen atom concentrations, low ion levels and relatively large Doppler effects, respectively. As far as the source is concerned both pressure and particle temperature are known to be low compared with conditions behind the shock so that the source line can be assumed to be thin compared to the absorbing

line. The error introduced if this latter assumption is not valid has been discussed quantitatively in Ref. 24 for conditions comparable with the present and is shown to be approximately 10% so that it also can be neglected in this initial study.

The only other possible source of error in the spectroscopic calculations is that due to a shift in frequency and asymmetry of Lyman α with pressure. The effect has been shown²⁴ to be small, of the order of 5 to 10% under conditions similar to the present, and is also neglected for the present.

On the basis of the foregoing, the absorption coefficient $k_{0\omega}$ of Lyman α radiation from the source by the ground-state hydrogen atoms behind the shock wave can be accurately calculated:²³

$$k_{0\omega} = k_0 \frac{a'}{\pi} \int_{-\infty}^{\infty} \frac{e^{-y^2} dy}{a'^2 + (\omega - y)^2}$$

$$\omega = \frac{2(\nu - \nu_0)(\ln 2)^{1/2}}{\Delta \nu_D} \quad \underset{\nu = \nu_0}{=} \quad 0$$

$$a' = \frac{\Delta \nu_N + \Delta \nu_L}{\Delta \nu_D} (\ln 2)^{1/2}$$

$$y = \frac{2\delta}{\Delta \nu_D} (\ln 2)^{1/2}$$

where k_0 is the absorption coefficient at the line center for the case of Doppler broadening only and is given by

$$k_0 = 8.51 \times 10^{15} \frac{f M^{1/2}}{\nu_0 T_2^{3/2}}$$

for a partial pressure of hydrogen atoms of 1 atmosphere.

The details of the experimental application of these principles are described in the next section; first, with respect to the development of

the light source and second, in terms of the adaptation of the light source and optical system to the shock tube.

III. EXPERIMENTAL

Development and Evaluation of the Light Source

A major portion of the experimental effort was devoted to the development of the narrow-line Lyman α (1215.7 \AA) source of sufficient intensity to provide a satisfactory signal-to-noise ratio at the detector after adaptation to the shock tube. The initial concept of the source was one of low total pressure and minimum thermal excitation to insure the emission of a narrow Lyman α line. Thus in the preliminary design of the source, the total pressure was held below 2 mm Hg and the means of excitation was 30 to 35 mc radiofrequency (RF) radiation. In addition, provision was made for dilution of the hydrogen with a noble carrier gas to counteract loss of energy by recombination and self-absorption effects. The implementation of these concepts resulted in the construction and testing of the following three source configurations.

Static Source with Lithium Fluoride Windows

This, the initial source, was intended primarily to check the effectiveness of the 30-35 mc RF discharge for excitation of Lyman α . The source consisted of a 12 mm i. d. pyrex pipe with a sealed lithium fluoride window 20 mm in diameter and 1.5 mm thick. The RF energy was applied to the discharge tube by means of two parallel-plate copper electrodes external to the tube which was filled with hydrogen and helium at desired static pressures.

The spectral emission of the source was detected at the exit slit of the monochromator by means of an RCA 1P21 photomultiplier coated

with sodium salicylate. The visible fluorescence of the coating provided a means of detecting the VUV radiation. The output of the photomultiplier was indicated on a recording potentiometer.

Interpretation of the data obtained from this source was difficult due to a significant decrease in the transmission of the LiF window with running time of the discharge. The major cause of the signal deterioration was attributed to the deposition of hydrocarbons from the window sealants effused and deposited via the discharge and to other compounds arising from discharge bombardment of the tube walls. The maximum Lyman α intensity obtained with a new LiF window was so low with respect to ultimate requirements that further work was abandoned on sources in which discharge contacted the LiF window.

Open-tube Windowless Source

A windowless source was constructed to investigate the feasibility of applying differential pumping by replacing the LiF window with a pressure gradient resulting from the expansion of the gas from the source into a vacuum chamber. Since the conductivity of the excited gas in the RF field is greater in the higher pressure regions of the source, the pressure gradient at the exit serves as an aerodynamic window which prevents the discharge from extending beyond the opening into the vacuum chamber. However, the large gradient allows the Lyman α radiation to pass through the low density, expansion region on the vacuum side of the opening with minimum attenuation due to self-absorption. In the initial source of this type the spectrometer entrance chamber was used to effect a pressure gradient between the source tube and the main spectrometer vacuum chamber.

The source tube consisted of a 10 mm i. d. pyrex tube, 20 cm long, the open end of which was placed approximately 3 mm from the monochromator entrance slit. The other end of the tube was connected to the source-gas metering system. In operation a mixture of hydrogen plus carrier gas was allowed to flow through the monochromator entrance slit whence it expanded into the main vacuum chamber in which a vacuum was maintained by a high capacity diffusion pump. The gas was excited by applying 30 to 35 mc RF radiation to two external ring electrodes which were spaced 15 cm apart with the front electrode positioned 10 mm from the spectrometer entrance slit. The source tube was cooled by a high velocity, dry air stream directed at the electrodes to dissipate the heat caused by the discharge.

In this type of source, the excited molecules and atoms from the discharge flow through the monochromator entrance slit and expand into the main vacuum chamber of the monochromator. Therefore, a slight possibility of damage to the MgF_2 coated grating existed. However, careful monitoring revealed no significant loss of grating reflectivity either at 1800\AA or at 1215.7\AA . The Lyman α signal obtained from this source was 60 times more intense than that from the previous static source.

Final Windowless Source

In principle this source, to which all succeeding discussion pertains, is the same as the open-tube source but was modified by the addition of a 1 by 10 mm slot at the emitting end of the source tube. This slot served as the aerodynamic window and also minimized contact of the discharge with the monochromator slit jaws. The source tube was

constructed from a 30 cm length of 10 mm i. d. medium-wall quartz tubing which was sealed and then slotted at one end in a manner to produce a flat, uniform slot. The source tube was attached to the VUV monochromator with an "O" ring-sealed mount which placed the slotted end about 3 mm from the entrance slit jaws with the slot parallel to the monochromator slit. In this position, the source energy radiated through the slot more than filled the acceptance angle of the monochromator. In operation, the gas flowing through the source passed through the slot and was partially expanded into the slit antichamber whence it was pumped through the monochromator slit.

The choice of electrode configuration represented a somewhat arbitrary compromise between source intensity and dielectric heating of the source tube. Flat plate electrodes above and below the source tube produced a uniform discharge of low intensity which spread over a large region of the source. Coiled copper tubing electrodes while producing a high source intensity caused severe dielectric heating. The ring or band electrodes were chosen because the RF field strength and thus the dielectric heating between electrodes could be controlled by a simple adjustment of their separation. After trying all promising combinations of connecting two electrode and three electrode systems to the transformer secondary, the three electrode system (in which the front and rear bands were connected to the secondary terminals with the middle electrode grounded) was found to produce almost twice the Lyman α intensity obtained with the two electrode systems.

The 3/4 in. i. d. by 1/4 in. wide copper band electrodes were made from flattened copper tubing with the ends silver soldered together to produce a smooth band with rounded edges. The electrode spacing of 5 cm between front and middle electrodes with the rear electrode 10 cm from the middle was selected to give maximum Lyman α intensity with a dielectric heating rate which could be counteracted by cooling the region near the electrodes with a dry air stream. The electrodes were concentrically suspended by three asbestos blocks wedged against the source tube to allow the dry air stream to flow between the electrodes and the source tube where most heating occurred.

The 30 to 35 mc RF energy was supplied by a 200 watt oscillator of the commercial dielectric heating type which was coupled to the source electrodes through a coaxial transmission line terminated in a balanced isolation transformed coil. The impedance of the transformer secondary coil was designed to provide reasonably good energy transfer for a range of load impedances. The RF energy delivered to the discharge was not measured quantitatively due to the difficulty of defining the impedance of the quasi-plasma discharge and electrode configuration. It is quite probable that only a fraction of the RF oscillator power was transmitted to the source discharge.

The spectrum in the Lyman α region emitted from pure hydrogen in the final source is shown in Fig. 2 for a manifold pressure of 0.5 mm Hg. The resolution of the spectrometer, which will be described later, is of the order of 2 to 3 Å in the 1200 Å spectral region. The wavelengths identified as molecular hydrogen bands are in good agreement with the

bands observed by Dieke²⁷ and Herzberg.²⁸ The intensity of the molecular bands increases as the source pressure is increased while the Lyman α intensity remains nearly constant, due to increased concentration of molecular hydrogen. The bands are absent when helium is used instead of hydrogen at the same source pressure, thus eliminating the possibility that these bands might be due to impurities removed from the source tube walls by the discharge.

The ratio of the $1218\text{\AA} \text{H}_2$ band intensity to the Lyman α for this source is 8% which may be compared with 30 to 50% for a typical direct current capillary discharge source²⁹ where strong thermal excitation is present. The intensity of the 1218 molecular band is important in this application due to its inclusion in the 8\AA spectral bandpass used in picking up Lyman α . This bandpass resulted from the wide slits used in order to obtain energy from a larger area of the source. Addition of helium carrier gas suppresses the effect of the molecular band to less than 0.5% as shown in Fig. 3. In the final source configuration where the discharge was confined at a manifold pressure of 3 mm Hg the ratio is less than 0.1%. As will be shown later, the spectral purity of the Lyman α radiation is further proven in the shock tube experiments by the complete absorption of its radiation by the hydrogen atoms behind the shock.

The performance of the source for helium and argon carrier gases as a function of manifold pressure measured at a distance greater than 100 cm from the source is shown in Fig. 4 for a constant partial pressure of hydrogen. As might be expected, the lighter helium carrier gas does not produce as much deexcitation and recombination of H atoms by collision as

does the argon. Thus a higher Lyman α intensity is observed with the helium carrier gas. At a manifold pressure above 2.5 mm Hg, the linear flow velocity in the source causes the discharge to confine between the front electrodes as shown in Figs. 4 and 5B with a marked increase of 1.5 times the intensity observed with the diffuse discharge shown in Figs. 4 and 5A. The most plausible explanation for the confinement is that the high linear flow velocity (approximately 500 cm/sec) in the source sweeps the ions which are formed between the two rear electrodes into the region of the front electrodes before deionization can occur. This produces in the gas a high conductivity which is then sustained by the strong RF field between the front electrodes. The appearance of the confined discharge was that of a pinkish-white glow extending from the source slot to the middle electrode as illustrated in Fig. 5B. It is of much lower intensity than the central, pinkish-white core shown in Fig. 5A for the diffuse discharge.

Since helium has a resonance line at $1215\overset{\circ}{\text{\AA}}$, the background spectrum of pure helium was scanned in the Lyman α region using the confined discharge and a manifold pressure of 3 mm Hg. The $1215\overset{\circ}{\text{\AA}}$ helium line was observed at an intensity of less than 1% of the Lyman α intensity for the conditions shown in Fig. 5B.

The effect of hydrogen concentration was examined for confined discharge at a manifold pressure of 3 mm Hg and was found to result in a rather broad maximum in the region of 20 to 25% as shown in Fig. 6.

Thus after optimization of the various parameters discussed, the Lyman α intensity of the final source as used in the shock-tube

experiments yielded a signal of adequate intensity with a signal-to-noise ratio of 30 at the detector when operated at a manifold pressure of 3 mm Hg and a partial pressure of H_2 of 0.5 mm Hg. Compared with the initial LiF-window source, this represents an increase of 1500 times in Lyman α intensity.

Adaptation of the Light Source to the Shock Tube

For the shock tube experiments, it was necessary to pass the radiation from the source through the shock tube and then into the monochromator. Adapting the source directly to the shock tube presented some difficulties because of space limitations. Figure 7 shows the source mounted to the shock tube wall. Since the source tube had to be quite close to the shock tube window in order to minimize light losses, the most serious design consideration involved the problem of window deterioration. LiF windows are susceptible to a deterioration effect known as "solarization" which is brought about by strong ultraviolet radiation or contact with ions. Since solarization leads to a severe loss of transmission in the vacuum ultraviolet, a great effort was made to avoid it. Subsequent discussion describes the design in terms of this and other problems.

Light Source

The source tube, as previously described, was of fused quartz with the discharge end sealed except for a 1 mm x 10 mm slot. In order to minimize losses due to self-absorption effects, the radiation from the slot must encounter as little atomic hydrogen as possible. To accomplish this, a low pressure expansion chamber was provided between the slot and the shock-tube window which allowed the molecules, atoms, ions and electrons

emerging from the source slot to diffuse radially as much as possible. This radial diffusion prevented any part of the discharge which protruded downstream of the slot (see Figure 5-B), from being too concentrated near the window. Pressure measurements made at the expansion chamber and far upstream in the source tube indicated that a tenfold pressure drop was achieved across the source slot. Source tube pressure and gas flow rate were controlled with a throttle valve.

The LiF window was also protected to a large extent by the slit plug which sealed it to the shock tube by means of a Viton "O" ring. The mean free path of hydrogen and helium is less than 1 mm at the pressure maintained in the expansion chamber (approximately 0.7 mm Hg). Since the window slit plug was thicker than several mean free paths, it also helped prevent ions, excited atoms and molecules from reaching the window. This mounting arrangement which sealed the window with a Viton "O" ring greatly facilitated the changing of windows when necessary.

The quartz tube was mounted in the lucite wall with a Viton "O" ring thus providing a vacuum tight seal between the expansion chamber and the electrode chamber. It also allowed the distance between the source tube and the window to be adjusted so that window deterioration could be further reduced, if necessary, by pulling the source tube back. However, in practice very little window deterioration was encountered so that the source tube was pushed to within a few mm of the window.

One of the problems compounded by the adaptation of the source to the shock tube is that of good RF coupling between the electrodes and the plasma. As previously discussed, good coupling is necessary in order to

obtain high Lyman α source intensity. To achieve this effect, the RF electrodes must be placed as close to the plasma and as far from metal walls and parts of the shock tube as possible. In spite of the above requirements, the source must be as close to the shock tube as practicable in order to illuminate as completely as possible the collimating system defined by the two shock tube window slits. The short optical path also reduces recombination effects. Unwanted RF coupling with the shock tube and nearby metal parts was minimized by using materials of high dielectric strength between the RF electrodes and the metal environment. Lucite was employed in the source tube mount because of its high dielectric strength, transparency and ease of machining.

The quartz source tube, electrode rings and lucite walls were cooled by a jet of air directed so as to form a high speed air vortex around the forward portion of the source tube. It is this forward portion of the source tube in the vicinity of the "O" ring gland and the first electrode, where RF heating can be least tolerated.

Shock Tube

The shock tube used imposed several conditions on the experiment. The tube, the only one of rectangular cross section available, had been fabricated several years previously by welding together steel plates to form the four walls which were further strengthened by angle irons continuously welded lengthwise over the outside corners. The rectangular cross section had inside dimensions of 1 1/2" x 2 1/2" and a 3/4" wall thickness. The entire driven section was made up of sections of this type except for the short test section to which the source was mounted. The

test section was fabricated by welding a stainless steel plate to the open side of a stainless steel piece having a $1\frac{1}{2}'' \times 2\frac{1}{2}''$ slot machined lengthwise along one side. All of the above sections were joined together by "O" ring-sealed flanges.

Due to the method of construction, the shock tube had virtual leaks which led to considerable outgassing and the welds had a tendency to develop small leaks when subjected to the pressure pulses that occur during shock runs. Because of these conditions, the shock tube had a leak-rate of approximately 1 micron/minute and could not be pumped down to less than 0.1 micron. This condition had a noticeable effect on the gas purity. The extent to which it influenced our data will be discussed later in the report.

Notwithstanding the aforementioned factors, the tube did serve to demonstrate the feasibility of the experiments and provided data from which rate constants could be calculated. Furthermore, the rectangular cross section of this shock tube made it ideal for optical absorption work, since it permitted the use of flat windows nearly flush with the inside walls. This configuration provided a practically constant optical path length across the tube and avoided the cylindrical lens effect that would have been present if a circular shock tube with curved windows had been used.

The Total System

The entire system including the gas-metering and vacuum pumping system is shown along with the more pertinent electronic apparatus in Fig. 8. Hydrogen and helium entered the system through rotameter-type flow meters and were metered into the source tube through calibrated-leak valves. The metering system and source tubing were purged prior to initiating source

flow by means of a liquid nitrogen-trapped glass vacuum system. This vacuum system was valved off when the flow was started. A Hastings vacuum gauge located along the gas delivery line was used to measure the pressure of the gas being delivered to the source. This pressure was somewhat higher than the actual pressure of the discharge but not by more than 1 mm Hg or so.

A liquid nitrogen cold trap was provided in the source tubing to eliminate any traces of water vapor or other condensable contaminants from the source gas. After passing through the RF excitation zone of the source and out into the expansion chamber, the gas was pumped by the spectrograph vacuum pump through the throttle valve and a liquid nitrogen cold trap. This cold trap prevented traces of cracked pump oil from reaching the LiF window. It was found early in this work that cracked pump oil led to rapid window deterioration apparently by augmenting the normal solarization process.

The beam of Lyman α radiation emitted by the discharge was defined by the window slits and focussed on the entrance slit of the spectrograph by a MgF_2 coated aluminum mirror in an evacuated chamber. The geometry of this mirror system was so chosen that one of its conjugate points lay at the center of the shock tube between the two LiF windows while the other was located at the entrance slit of the spectrograph. In this way, all of the light emerging from the second shock tube window was brought into the spectrograph and completely filled the grating. This resulted in the best compromise between radiation economy and shock front resolution by keeping the beam as narrow as possible.

The vacuum ultraviolet monochromator made it possible to separate the Lyman α radiation from the unwanted radiation produced by the source tube and the shock-heated test gas. A MacPherson Model 230-S vacuum ultraviolet monochromator employing a 1200 line per mm, MgF_2 -coated, concave grating was used with a 15° exit tube. The entrance and exit slits were 1 mm and 0.5 mm wide respectively, inasmuch as the resonance line technique used herein allows the use of wide slits. Lyman α radiation emerging from the exit slit was detected by means of the fluorescence from a sodium salicylate coated EMI 9558B end window photomultiplier.

The absorption measurements resulting from the passing shock front were recorded on an oscilloscope. The oscilloscope was triggered by the signal obtained from shock wave pickup No. 1 while the digital timer recorded the shock wave travel time at each of the three shockwave pickup stations. The shock velocities and consequently shock temperatures were obtained from these measurements.

IV. RESULTS AND DISCUSSION

The Data and Their Reduction

The final shock-tube source configuration yielded a Lyman α output similar to that of the configuration in which the source was connected directly to the spectrograph. The gas pressure required for good discharge confinement and optimum Lyman α output was approximately the same as for the previous sources (5 to 7 mm Hg). Also, the proportion of hydrogen needed in the helium mixture for optimum brightness, between 8% and 10%, was also similar to the earlier sources.

Window deterioration was effectively minimized so that only one change of windows was required during the entire course of the tests; a window change was deemed necessary only when its transmission had dropped by 50%.

The operational signal-to-noise ratio was not too favorable primarily because of problems with the photomultiplier tube and the fact that the source intensity was not sufficiently intense to overcome the additional light losses incurred in adapting it to the shock tube. Due to mechanical damage or age, the photomultipliers developed excessive shot noise. The laboratory program was temporarily terminated awaiting renewal before new photomultipliers could be installed. In spite of these adverse factors, the absorption of the Lyman α radiation by atomic hydrogen resulting from dissociation in the shocked test gas was very evident.* However, without electrical filtering of the

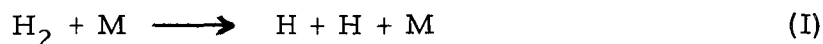
* A test carried out under identical shock conditions, but using only argon as a test gas showed no evidence of attenuation (See Figure 11).

photomultiplier output, the signal-to-noise ratio was too low to yield reliable shock-tube reaction rates. For example, Fig. 9 indicates a relaxation time τ_r (time for signal to reach $1/e$ of I_0) somewhere between 25 and 125 microseconds. The presence of excessive tube noise prevented a better estimate from being made since the noise pulses could not be adequately averaged out in the portion of the trace where the absorption was changing at the highest rate.

By increasing the photomultiplier load resistance, it was possible to filter out most of the electronic noise with a corresponding sacrifice in detector response time. Figures 10 through 12 show filtered data taken under conditions similar to those corresponding to Fig. 9. The filter time constant $\tau_f (= RC)$ was 282 microseconds in Fig. 1 and the relaxation time constant τ_r less than 100 microseconds. Even though the I/I_0 data suffer a time distortion due to the filter, it was still possible to compute τ_f from the filtered data since we know the true form of I/I_0 . Appendix I describes the technique used to compute τ_r from the filtered scope data. Figures 10 and 11 were taken under almost identical shock conditions. Helium was used as a driver gas at 117 psig with the driven gas consisting of 1% hydrogen in argon at a total pressure of 45 mm Hg. Figure 12 was obtained with a helium driver pressure of 71 psi and a driven pressure of 15 mm Hg consisting of 0.082% hydrogen in argon. The table below shows time constants calculated in the manner indicated. Also given are the shock temperatures obtained from CAL IBM computations.²⁹

TABLE I			
Figure	Shock Velocity	τ_r	Gas Temp. ($^{\circ}$ K)
10	1.26×10^5 cm/sec	70 μ sec	1675
11	1.27×10^5 cm/sec	74 μ sec	1710
12	1.45×10^5 cm/sec	155 μ sec	2145

From these data, preliminary values of the specific dissociation rate constant, k_d were calculated for the reaction



using the kinetic form

$$-\frac{d[\text{H}_2]}{dt} = k_d [\text{H}_2] [\text{M}]$$

From this, one obtains by integration

$$\alpha = 1 - c/c_0 = 1 - e^{-k_d c_M t}$$

The optical attenuation of Lyman α is given by

$$I/I_0 = e^{-k_{o,} P_H l}$$

where $k_{o,}$ is calculated as shown earlier in the report. In terms of the hydrogen atom concentration this becomes

$$I/I_0 = \exp(-646.5 k_{o,} k_d c_M^2 T_2 X_{H_2} t_p)$$

Letting

$$\chi = 646.5 k_{o,} c_M^2 T_2 X_{H_2}$$

k_d , in terms of the actual laboratory or oscilloscope time, becomes

$$k_d = - \frac{\bar{U} \ln I/I_0}{\chi t_s} \quad (1)$$

Values for k_d in cc/mole-second have been calculated; k_r has been calculated from the equilibrium constant:

TABLE II

Figure	T_2 °K	k_d	α_{τ_r}	$\frac{\alpha_{\tau_r}}{\alpha_{eq}} \times 100$	k_r
10	1675	1.06×10^4	2×10^{-5}	4.0	1.0×10^{17}
11	1710	1.01×10^4	2×10^{-5}	2.8	5.4×10^{16}
12	2145	4.66×10^5	7.5×10^{-4}	0.75	4.8×10^{15}

Here α_{τ_r} and α_{eq} are the fraction of the H_2 molecules dissociated at time τ_r and at equilibrium, respectively.

Interpretation

It will be noted that very small concentrations of H atoms are required for optical extinction. This essentially eliminates the necessity of considering the reverse reaction and implies virtual constancy of the initial concentration of H_2 . On the other hand, the small concentrations of H_2 used makes the reaction sensitive to catalyzing impurities as will be discussed in the succeeding material.

While these initial results must be considered preliminary, it has been of considerable interest to compare them with calculated and reported values. Comparison with k_d calculated from the collision theory equation using the dissociation energy of H_2 as the activation energy and a probability factor P of 1, shows the measured rates to be higher than those calculated, but by a factor which decreases radically with increasing temperature. This is shown in Table III (k_d in cc/mole-sec) and is also apparent from Fig. 1 where the k_r 's are compared with those from the current literature.

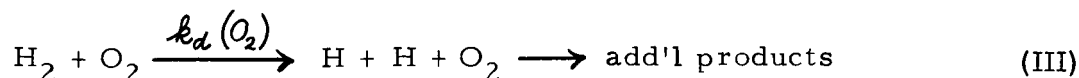
TABLE III

T_2 °K	k_d (exper.)	k_d (calc.)
1675	1×10^4	37
2145	4.7×10^5	4.2×10^4

The rapid decrease in the $k_d(\text{exper.})/k_d(\text{calc.})$ ratio with increasing temperature essentially precludes an explanation for the high value for k_d in terms of energy contributions from internal (vibrational and rotational) degrees of freedom. The (E/RT) terms could provide a factor of 2 at most for the change of the $k_d(\text{exper.})/k_d(\text{calc.})$ ratio over the temperature range involved. Furthermore, such an explanation seems unwarranted in view of the uncertainty extant in this type of theory, especially when one collision partner is a monatomic inert gas.

An explanation for the strong temperature dependence of $k_d(\text{exper.})/k_d(\text{calc.})$ has been found in terms of the presence of small amounts of oxygen known to be present in the tube at the time of shocking. This factor may also have contributed to the results from previous investigations. As mentioned in the experimental section, leak rates were carefully measured as the experiments proceeded so that it has been possible to make a good estimate of the total pressure of air in the tube at run time. The partial pressure of oxygen has been taken to be 2 microns in the succeeding considerations and is undoubtedly a reasonable value.

Basically, the consideration becomes one of comparing the rates of the following two reactions.



It is apparent that the H_2-O_2 reaction, chain-branching or explosive in nature, is offered little or no rate competition by the highly endothermic H_2-Ar reaction for given starting reactant concentrations, i. e.,

$k_d(O_2)/k_d(Ar) \gg 1$. The question here becomes only one of whether $k_d(O_2)/k_d(Ar)$ is sufficiently large to overcome the small value of the concentration-product ratio $[H_2][O_2]/[H_2][Ar]$.

To test this hypothesis, a value for $k_d(O_2)$ was calculated at the lower temperature from formula (1) using the known partial pressures of H_2 and O_2 , the latter obtained from the estimate described above. This gave the value of k_d listed in Column I of Table IV (k_d in cc/mole-sec). When this value is substituted in the collision theory equation along with the appropriate frequency factor and $P = 1$, an activation energy of 51,500 cal/g-mole (Column 2) results. This activation energy, when applied to reaction III at 2145°K provides the k_d of Column 3, 8.2×10^9 . This can then be compared with the experimental value of k_d obtained for these conditions by using Formula (1) as was done for Column 1. This gives the value of Column 4 which differs from Column 3 by a factor of 2, a considerably better agreement than in the case of $H_2 + Ar$ as also compared in Table IV.

TABLE IV

Reaction	Temp. (°K)	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
		k_d (exper.)	E_a (cal'd from Col. 1)	k_d (cal'd from Col. 2)	k_d (exper.)
III $H_2 + O_2$	1675	2.4×10^8	51,500		
III $H_2 + O_2$	2145			8.2×10^9	4.0×10^9
II $H_2 + Ar$	1675	1.06×10^4	85,500		
II $H_2 + Ar$	2145			3.1×10^6	4.7×10^5

It may be concluded from these considerations that one is dealing with a reaction of considerably lower activation energy than that of reaction II. Since these data must be considered preliminary they do not warrant extensive calculation of apparent activation energies for the complex $\text{H}_2\text{-O}_2$ system behind shock waves.^{31, 32} However, it is apparent that a marked lowering of activation energy must be expected compared to the $\text{H}_2\text{-Ar}$ system.

The effect of oxygen, in the amounts present, on the H_2 dissociation rate is not surprising in view of the small concentrations of hydrogen used in these experiments. The presence of oxygen could not be avoided with the shock tube used for these initial experiments; it does raise the serious question of the degree to which these and other data reported in the literature may have been similarly affected. This can best be answered by designing future experiments as indicated in the last section.

Conclusions

The experiments described in this report demonstrate the feasibility of following with great precision the rate of growth of atomic hydrogen behind shock waves by atomic resonance absorption spectrophotometry. Actual rates have been calculated from these data but must be considered preliminary because certain aspects of the experiments are subject to considerable improvement. While an effective, continuously operating source of the Lyman α line of atomic hydrogen has been developed, an increase in the intensity of the recorded signal is desirable for future experiments in order to increase the speed of response of detection of the signal output. It has also been shown that the presence of small

amounts of oxygen or air may catalyze the rates of dissociation of the hydrogen molecule. It is planned, therefore, that the continuation of this research will be carried out in a high purity shock tube to be constructed at CAL. The tube is designed specifically to control the amounts of all important gaseous impurities.

While the technique has thus far been limited to the study of the hydrogen atom, it is planned to explore the applicability of the technique to the measurement of the time-dependent concentration of oxygen and nitrogen atoms behind shock waves. In addition, it is believed that this application of a. r. a. s. to shock tube gasdynamics can be modified to permit measurement of considerably greater concentrations of atomic species. This would be achieved by using a line-source of Lyman α slightly removed in wave-length from the line center. The use of deuterium instead of protium as the source gas provides such a line.

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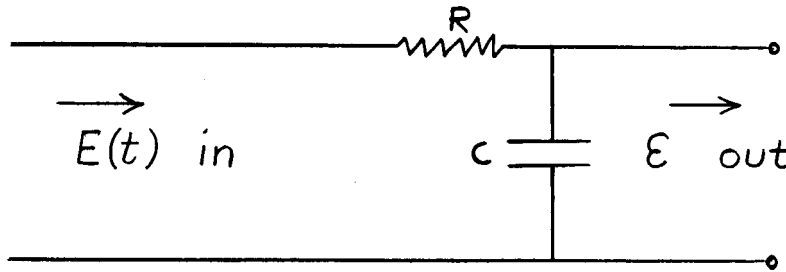
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APPENDIX I

Method of Computing τ_r from the Filtered Scope Data

When a signal of known form but underdetermined constants is operated on by a simple filter, the resultant signal can be analyzed to yield these signal constants if the filter constant is known. In the present case, the filter is a simple RC network that is formed by the capacitance and the load resistance of the photomultiplier cable and oscilloscope input circuit. The following diagram and differential equation describe the simple RC filter driven by the true shock tube transmission signal $E(t)$ (assumed to be initially decreasing exponentially with time) from the photomultiplier:



$$R \dot{q} + \frac{q}{C} = E(t) = E_o e^{-t/\tau_r} \quad (A-1)$$

where:

- | | | |
|----------|---|---|
| R | = | the total filter load resistance |
| C | = | the total filter capacitance |
| q | = | the charge stored by the capacitive elements |
| E_o | = | the maximum signal voltage (signal voltage before the shock occurs) |
| τ_r | = | the true time constant of the shock tube reaction signal |
| $E(t)$ | = | true input from photomultiplier |

In terms of the filter output signal voltage (that recorded by the scope) we may write:

$$\dot{\mathcal{E}} + \frac{\mathcal{E}}{\tau_f} = \frac{E_o}{\tau_f} e^{-t/\tau_r} \quad (\text{A-2})$$

where:

\mathcal{E}	=	the output signal voltage of filter (displayed on scope)
		= q/C
τ_f	=	RC, the time constant of filter

The solution of Eq. (A-2) is

$$\mathcal{E}(t) = E_o \left[e^{-t/\tau_f} - \frac{\tau_r}{\tau_f - \tau_r} \left(e^{-t/\tau_r} - e^{-t/\tau_f} \right) \right] \quad (\text{A-3})$$

E_o actually represents I_o (the light level in the absence of absorption) assuming that complete extinction takes place, which indeed occurs in our case as evidenced by the unfiltered data. $\mathcal{E}(t)$ represents the light intensity I_m , measured during absorption from the filtered scope trace photographs.

$$I_m/I_o = e^{-t/\tau_f} - \frac{\tau_r}{\tau_f - \tau_r} \left(e^{-t/\tau_r} - e^{-t/\tau_f} \right) \quad (\text{A-4})$$

τ_r can be computed by the method of iteration after Eq. (A-4) is cast in the form:

$$\tau_r = \frac{\tau_f \left[I_m/I_o - e^{-t/\tau_f} \right]}{I_m/I_o - e^{-t/\tau_r}} \quad (\text{A-5})$$

This is of the form

$$\tau_r = \phi(\tau_r) \quad (\text{A-6})$$

The real root can be found by substituting an approximate value of the root $\tau_r^{(0)}$ into the right-hand part of (A-6) to yield a better approximation

$\tau_r^{(1)}$ as follows:

$$\tau_r^{(1)} = \phi(\tau_r^{(0)})$$

This process is repeated in the manner

$$\tau_r^{(2)} = \phi(\tau_r^{(1)})$$

$$\tau_r^{(n)} = \phi(\tau_r^{(n-1)})$$

The above method of iteration will converge to the solution only if the derivative of $\phi(\tau_r)$ evaluated at τ_r satisfies the following condition:

$$-1 < \phi'(\tau_r) < 1 \quad \text{where} \quad \phi' = \frac{d\phi}{d\tau_r}$$

In our case, the derivative of (A-5) with respect to τ_r , $\phi'(\tau_r)$, meets the above condition so the process applied to (A-5) converges.

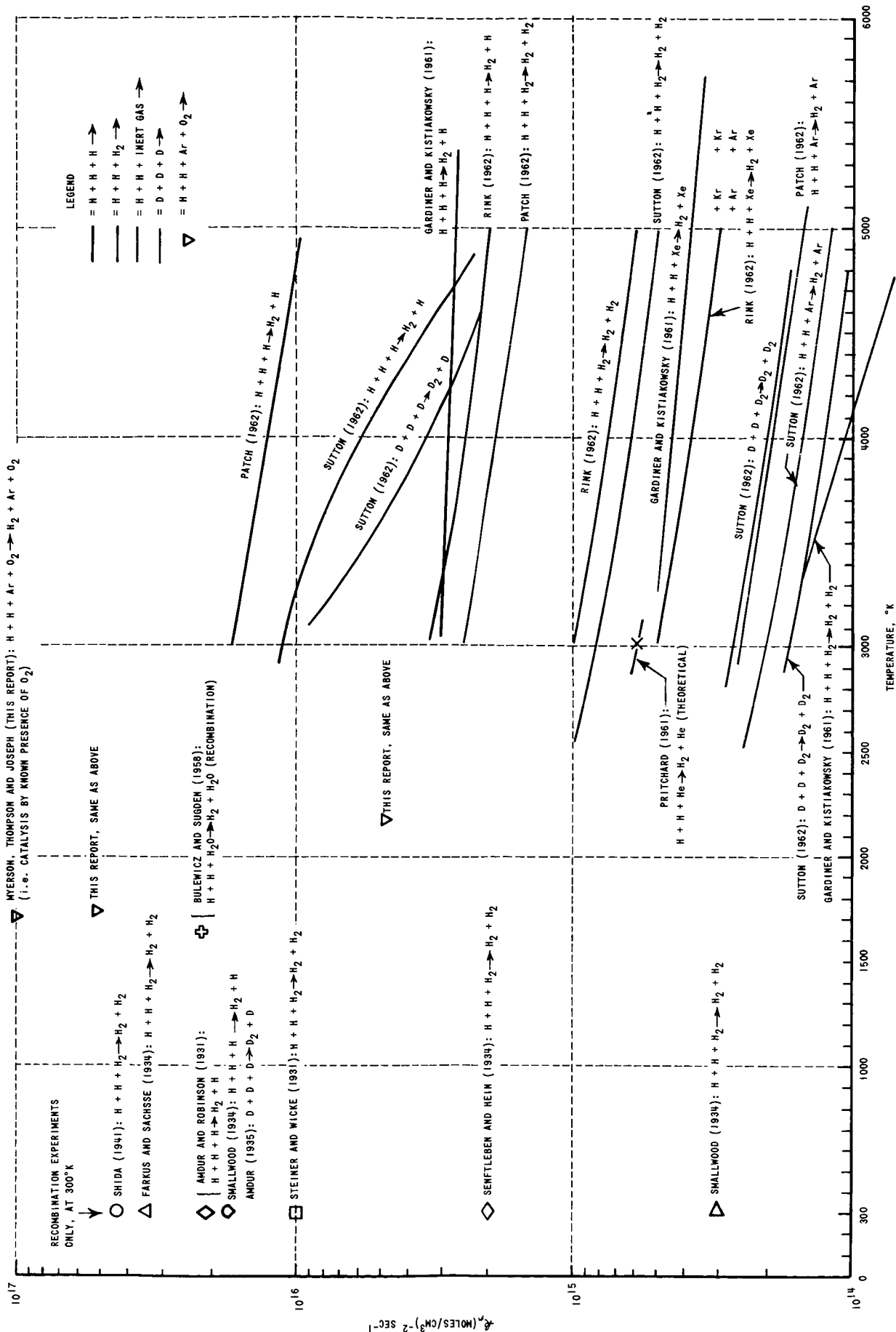


Figure 1 PRESENT STATUS OF OBSERVATIONS OF HYDROGEN DISSOCIATION IN TERMS OF k_p 300° TO 5000°K

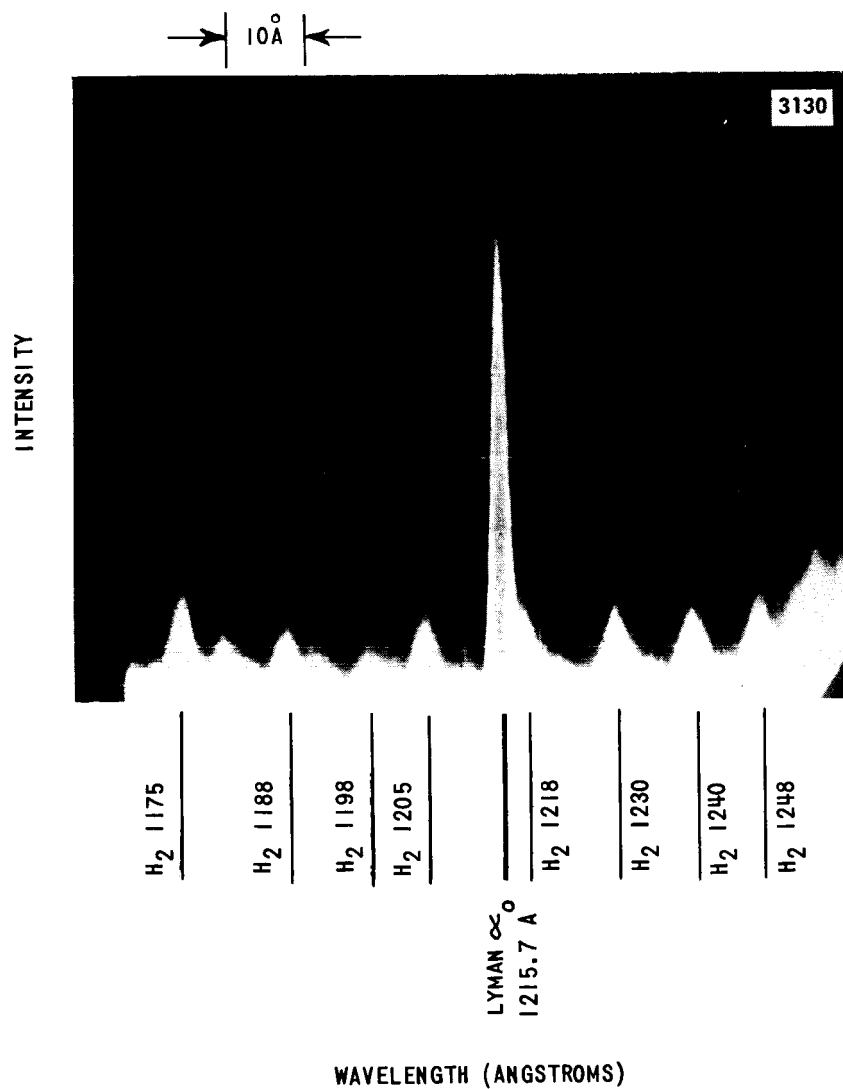


Figure 2 SPECTRUM OF WINDOWLESS SOURCE

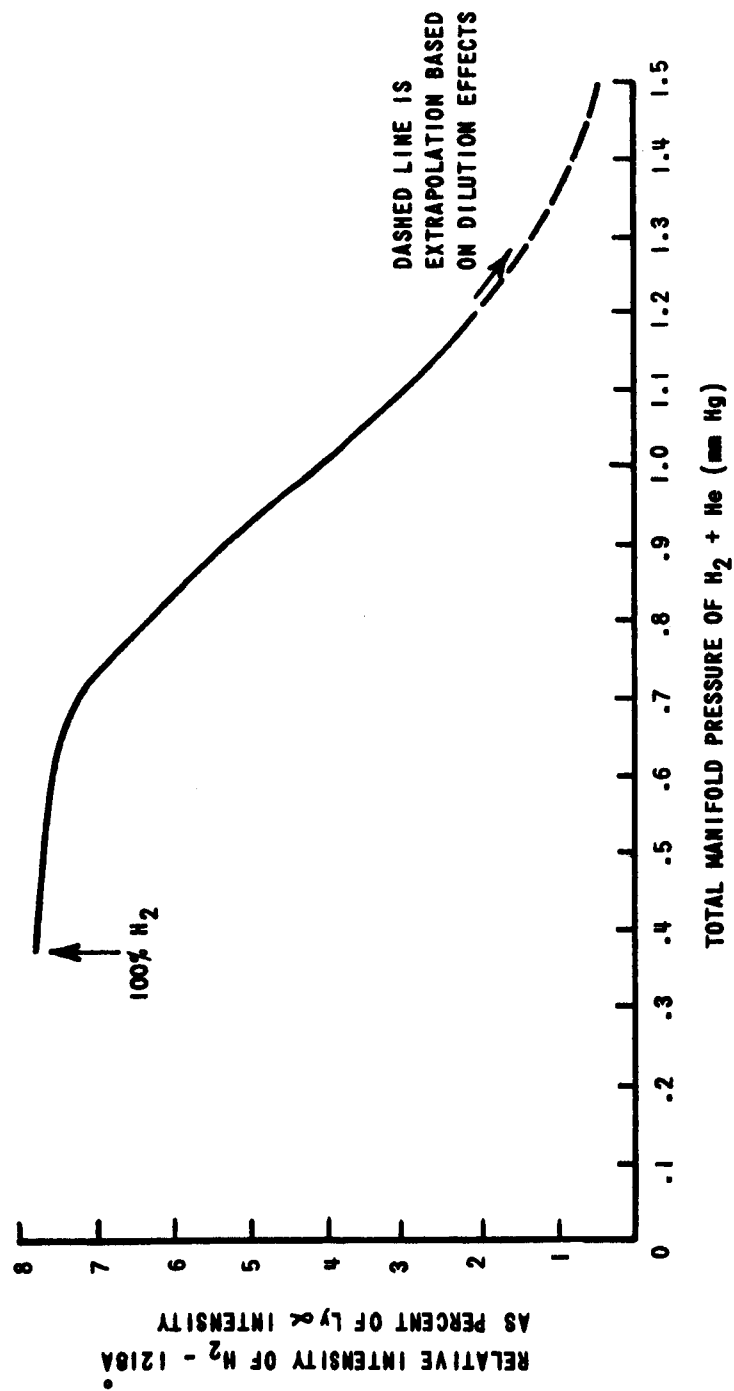


Figure 3 SUPPRESSION OF H_2 MOLECULAR BAND AT 1218 \AA BY ADDITION OF HELIUM CARRIER GAS

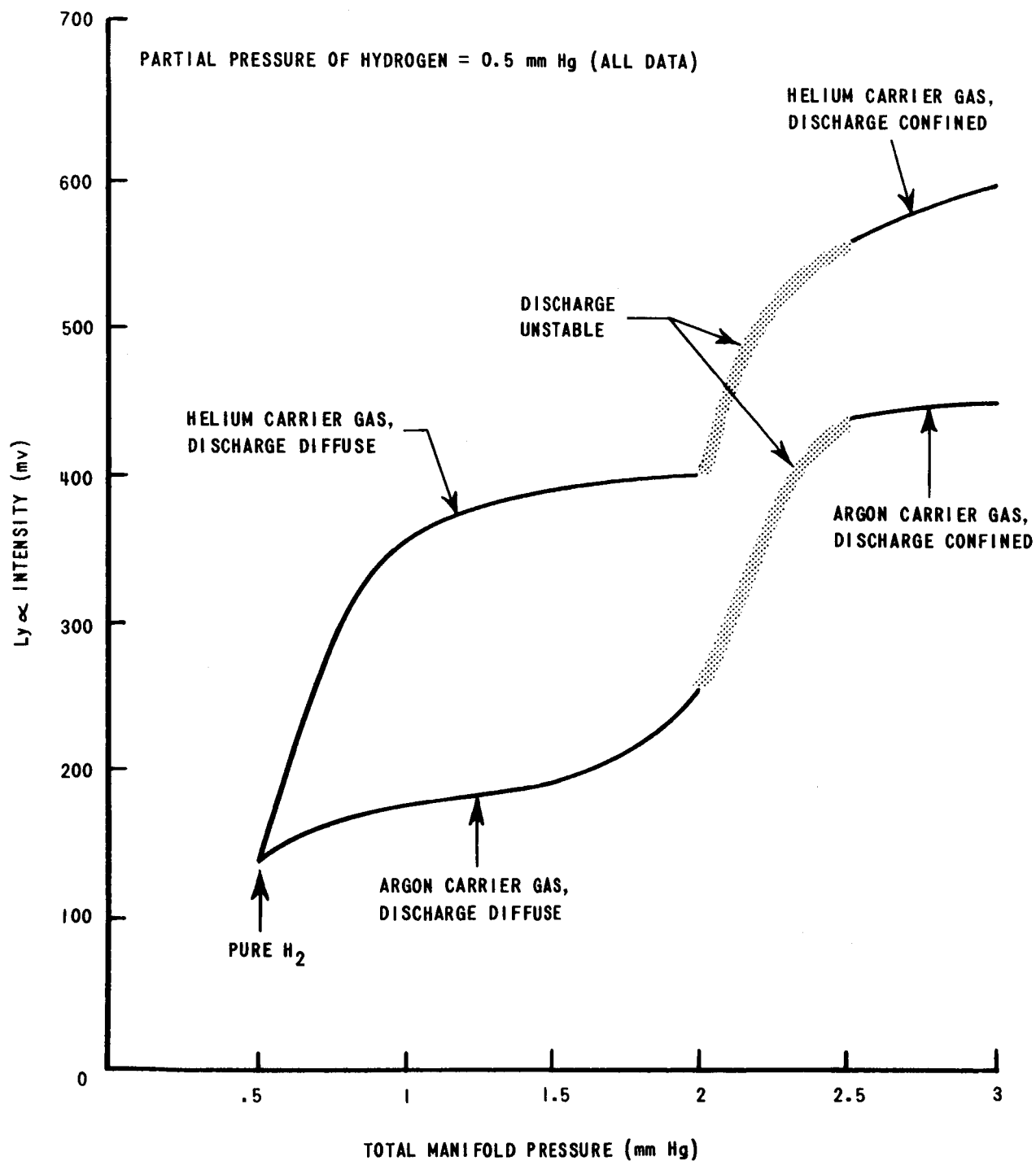


Figure 4 LYMAN α INTENSITY VS MANIFOLD PRESSURE FOR HELIUM AND ARGON CARRIER GAS AT CONSTANT HYDROGEN PARTIAL PRESSURE

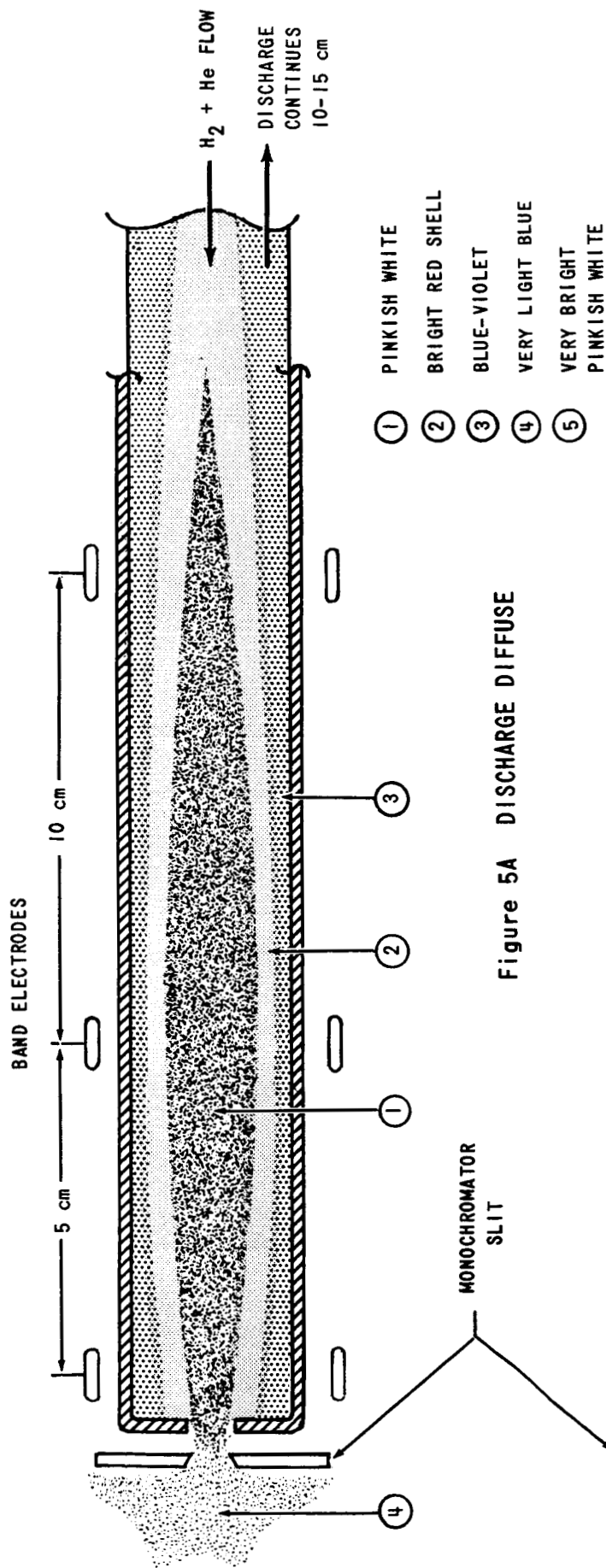


Figure 5A DISCHARGE DIFFUSE

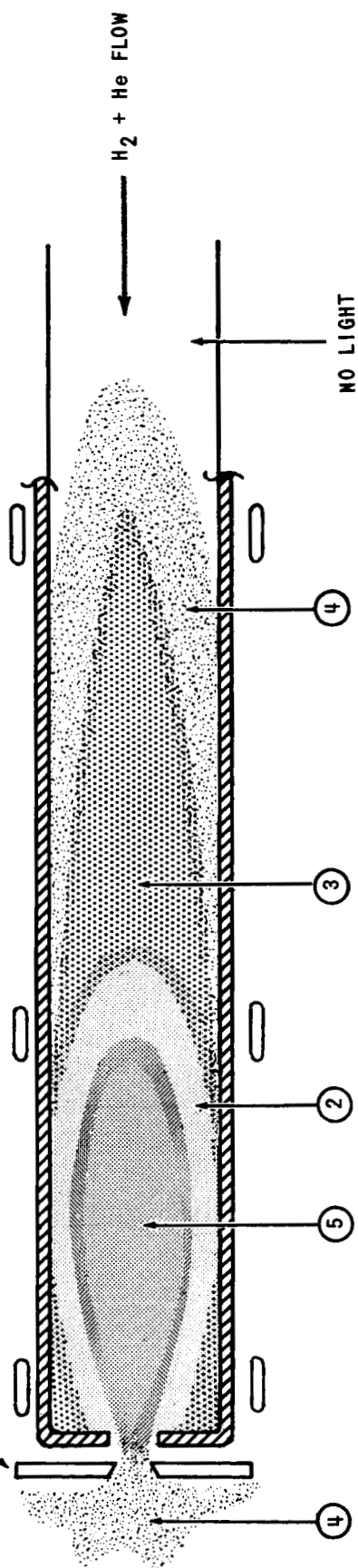


Figure 5B DISCHARGE CONFINED

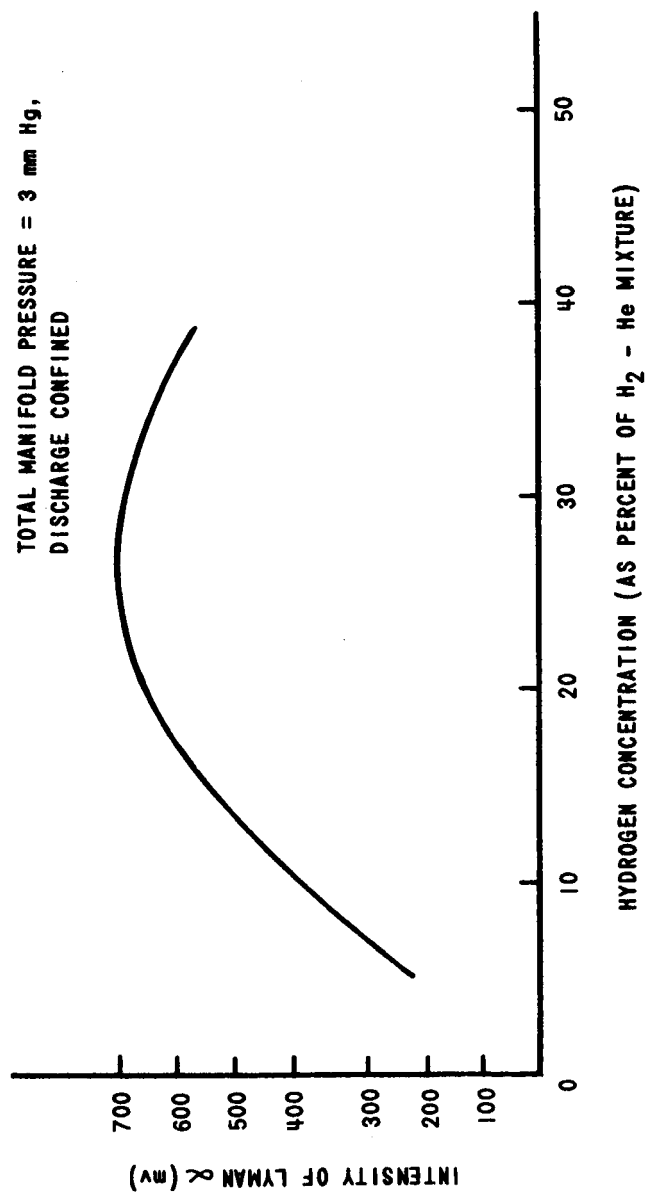


Figure 6 $\text{LYMAN} \propto \text{INTENSITY VS HYDROGEN CONCENTRATION}$

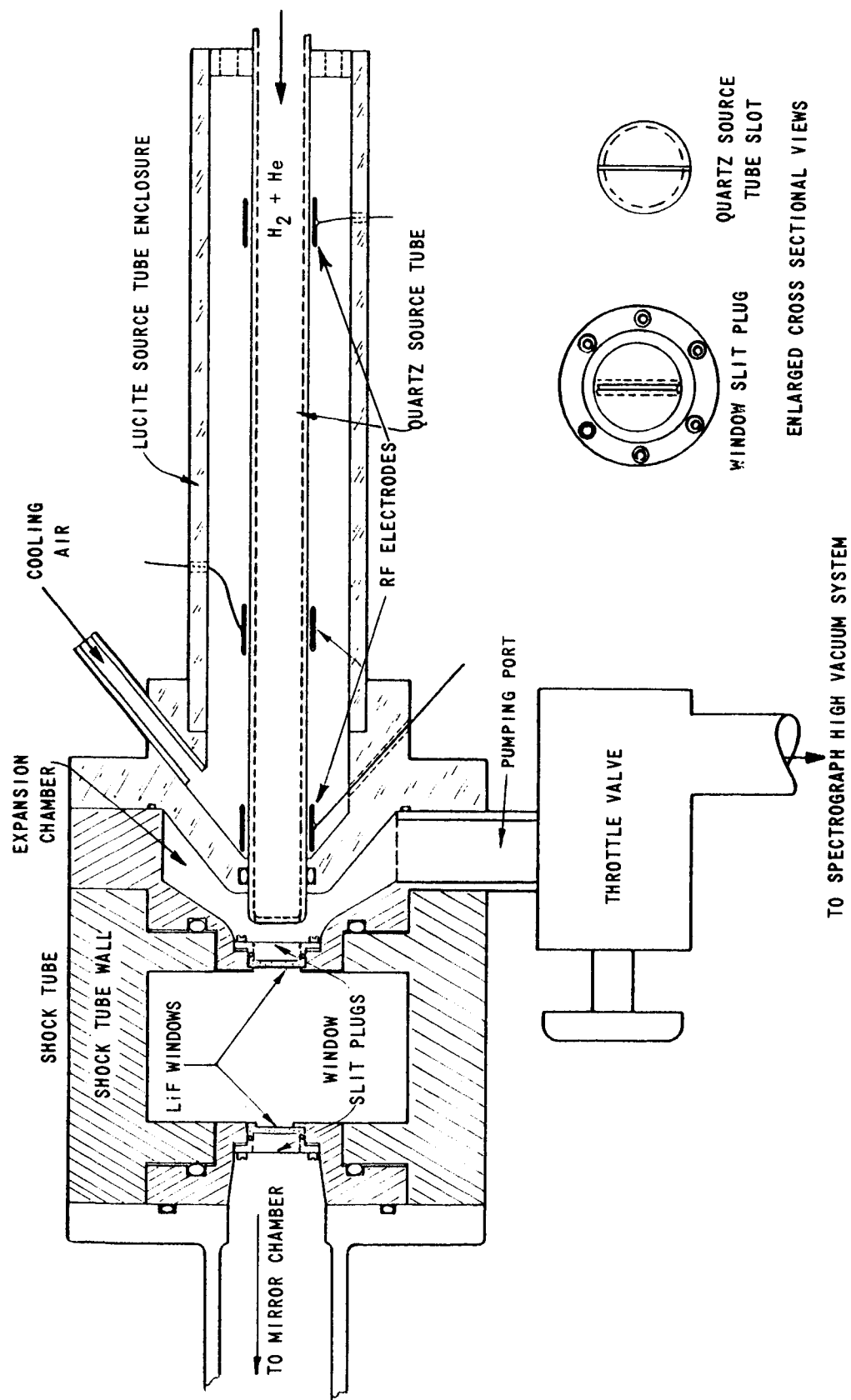


Figure 7 LYMAN α LIGHT SOURCE

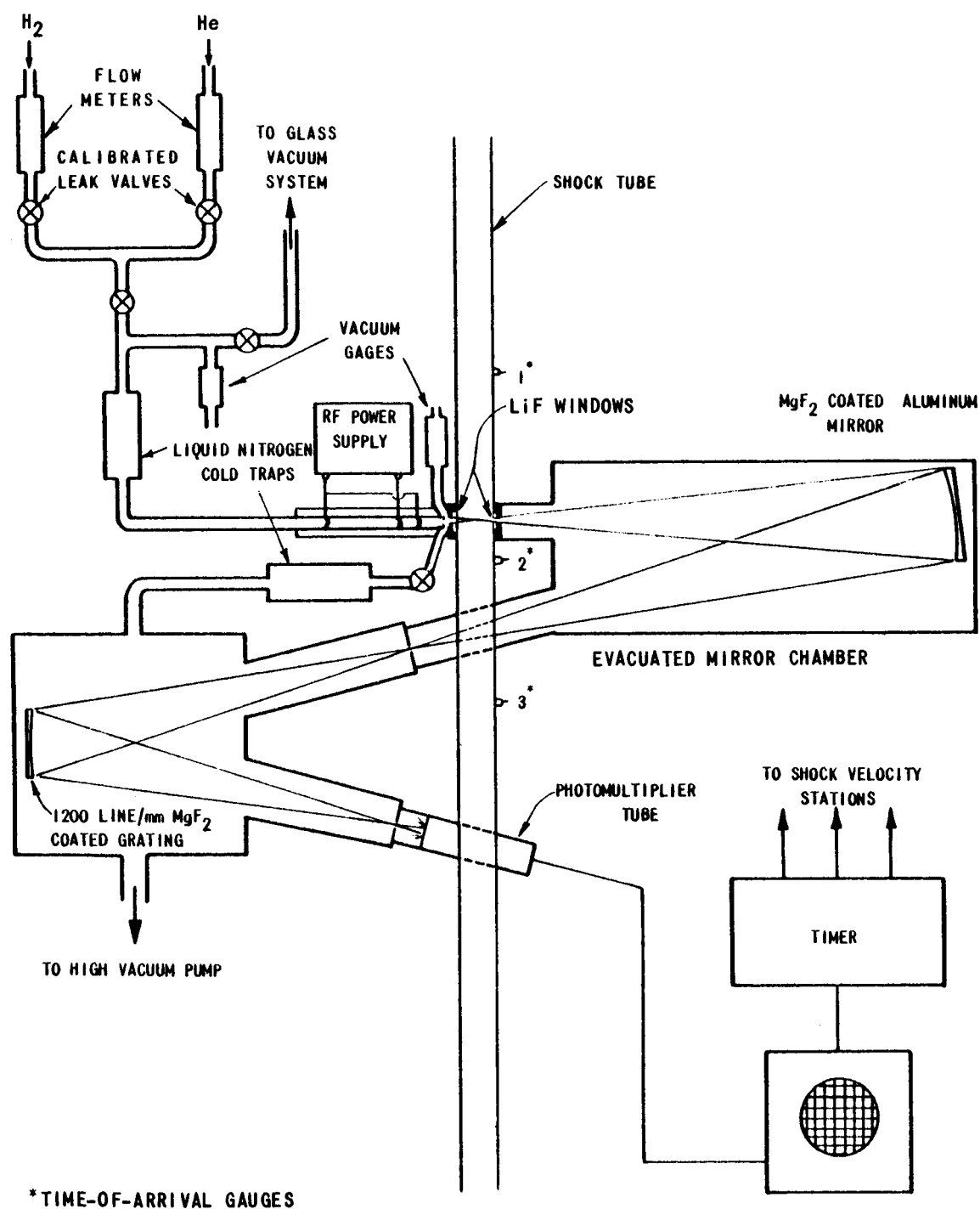


Figure 8 APPARATUS FOR MEASUREMENT OF ATOM CONCENTRATIONS BEHIND SHOCK WAVES

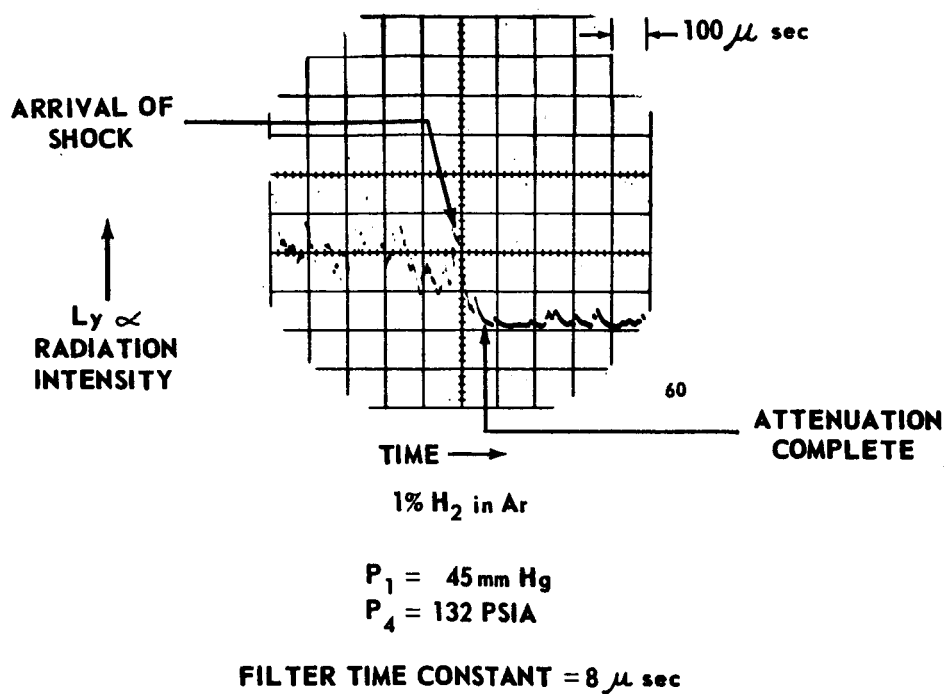


Figure 9 ATTENUATION OF LYMAN α RADIATION (1215.7A) BY H-ATOMS BEHIND A SHOCK-WAVE

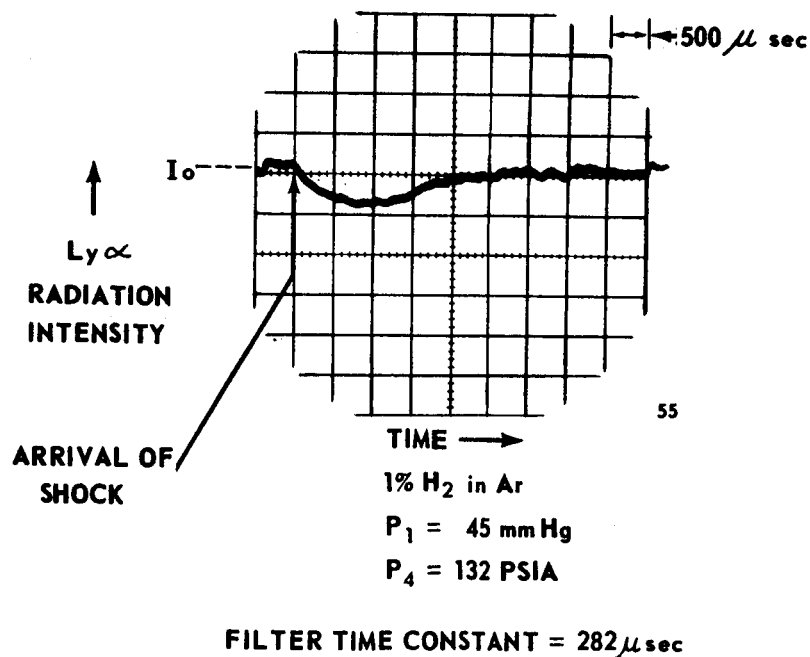


Figure 10 ATTENUATION OF LYMAN α RADIATION (1215.7A) BY H-ATOMS BEHIND A SHOCK-WAVE

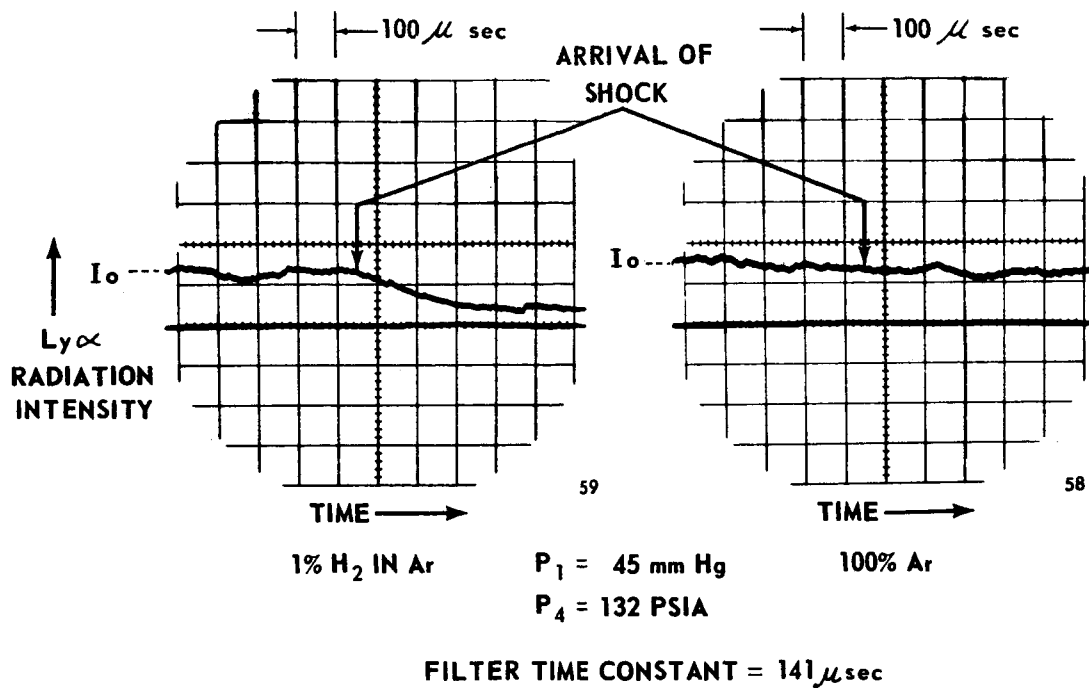


Figure 11 ATTENUATION OF LYMAN α RADIATION (1215.7 Å)
BY H-ATOMS BEHIND A SHOCK-WAVE

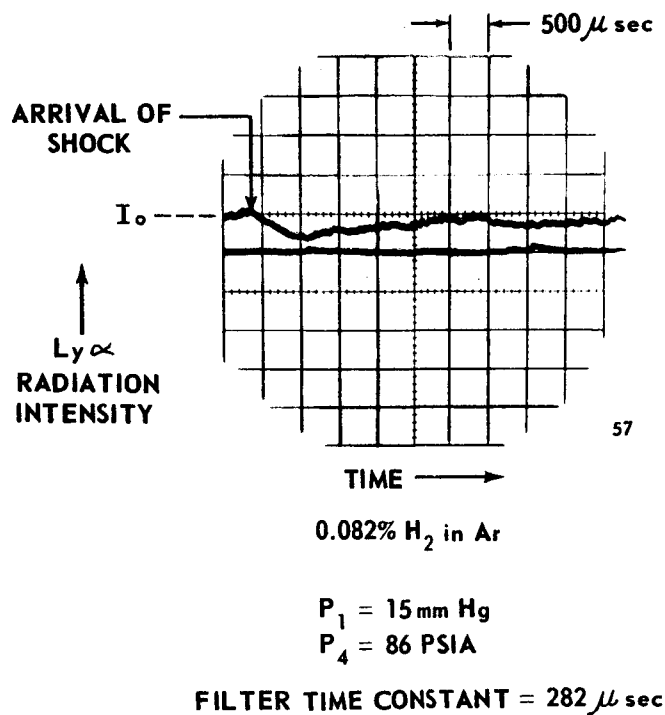


Figure 12 ATTENUATION OF LYMAN α RADIATION (1215.7 Å)
BY H-ATOMS BEHIND A SHOCK-WAVE